

# Electronic structure of the $\sigma$ -phase in paramagnetic Fe-V alloys. Experimental and theoretical study.

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The electronic structure of  $\sigma$ -phase  $\text{Fe}_{100-x}\text{V}_x$  compounds with  $33.3 \leq x \leq 60.0$  was calculated from the charge self-consistent Korringa-Kohn-Rostoker method. For the first time, charge densities  $\rho_A(0)$  and electric field gradients were determined at Fe nuclei, that occupy five nonequivalent lattice sites. The highest  $\rho_A(0)$  values were found on sites A and D, and the lowest one on site B, the difference ranging between 0.162 and 0.174  $s$ -like electrons per Fe atom for  $x = 33.3$  and  $x = 60$ , respectively. The calculated quantities combined with experimentally determined site occupancies were successfully applied to analyze  $^{57}\text{Fe}$  Mössbauer spectra recorded on a series of 8 samples in a paramagnetic state.

Studies of complex intermetallic phases, where several nonequivalent crystallographic sites exist, are of a great interest [1, 2, 3, 4]. Especially challenging in this context are disordered alloy systems with the complex structure such as  $\sigma$ -phases. The latter, whose archetypal example is that in the Fe-Cr system [5], belongs to an important class of tetragonal close-packed crystallographic structures [6] viz. the Frank-Kasper phases [7]. They are characterized by a high coordination number (CN), varying from CN=12 to 15 in the  $\sigma$ -phase. The unit cell (space group  $P4_2/mnm$ ) contains 30 atoms distributed in a non-stoichiometric way over 5 crystallographic sites, commonly labeled A, B, C, D and E. The importance of this class of phases is further reinforced by the fact, that they exhibit topological properties similar to simple metallic glasses due to an icosahedral local arrangement [8]. Consequently, they can also be regarded as very good approximants for dodecagonal quasicrystals [8]. Indeed, close similarity between vibrational properties of a one-component  $\sigma$ -phase on one hand and a one-component glass with the icosahedron local arrangement on the other, was recently reported [3].

The complex structure and a lack of stoichiometry also cause the interpretation of experimental results obtained for  $\sigma$ -phase samples to be a difficult task. Here, a  $\sigma$ -phase magnetism which can be found in some alloy systems like Fe-Cr and Fe-V is of a particular interest [9, 10]. In order to understand it properly, one should know sublattice magnetic properties. An access to the latter is experimentally possible with microscopic techniques such as Mössbauer Spectroscopy (MS) or Nuclear Magnetic Resonance (NMR). We are not aware of using NMR in studying Fe-containing  $\sigma$ -phases, but MS has been already applied and distinction between electronic properties of nonequivalent sites was not obtained due to low resolution in the measured spectra [9, 10]. However, backed by dedicated electronic structure calculations, relevant information on Fe charge-densities and electric field gradients (EFG) on all nonequivalent sites has been already provided in the case of the  $\sigma$ -Fe-Cr compounds in

a paramagnetic state [11].

In this Letter we report results obtained with similar calculations for the  $\sigma$ -phase in  $\text{Fe}_{100-x}\text{V}_x$  alloys, also in the paramagnetic state. This series of compounds is especially well-suited for verifying electronic structure computations, since a composition range of the Fe-V  $\sigma$ -phase existence is several times wider than that in the Fe-Cr system. The non-spin polarized KKR results have been used to analyze  $^{57}\text{Fe}$ -site Mössbauer spectra recorded at 295 K (paramagnetic state) in the  $\sigma$ -phase compounds  $\text{Fe}_{100-x}\text{V}_x$  with  $34.4 \leq x \leq 59.0$ .

The Mössbauer spectrum associated with each site can be characterized by the following spectral parameters: amplitude  $I$ , line width  $G$ , isomer shift (center of gravity),  $IS$ , that measures a charge-density at nucleus of the probe atom, and quadrupole splitting,  $QS$ , that gives information on the electric field gradient (EFG) in the lattice. Taking into account one parameter for a background and the fact that in the unit cell of the sigma there are five sites (sublattices) one needs 21 parameters to describe the overall spectrum. However, as the  $^{57}\text{Fe}$ -site Mössbauer spectrum of the  $\sigma$ -phase in the paramagnetic state has no well-resolved structure [10], unique determination of these parameters from the spectrum analysis itself appears impossible and additional information is required. The latter can be partly obtained e. g. from a neutron diffraction experiment that has not only confirmed the presence of the probe  $^{57}\text{Fe}$  atoms on all 5 sites but also yielded precise knowledge on their relative population on these sites [12]. Assuming the Lamb-Mössbauer factor to be site independent, the relative contribution of each subspectrum ascribed to the site should be equal to the corresponding values determined from the neutron experiment. Setting the latter as constraints, reduces the number of free parameters from 21 to 17 which is still to high to allow the unique refinement of the spectrum. Theoretical calculations, as those presented elsewhere, are of a great help in this respect [11].

It seems that the KKR method combined with the coherent potential approximation (CPA) would be best

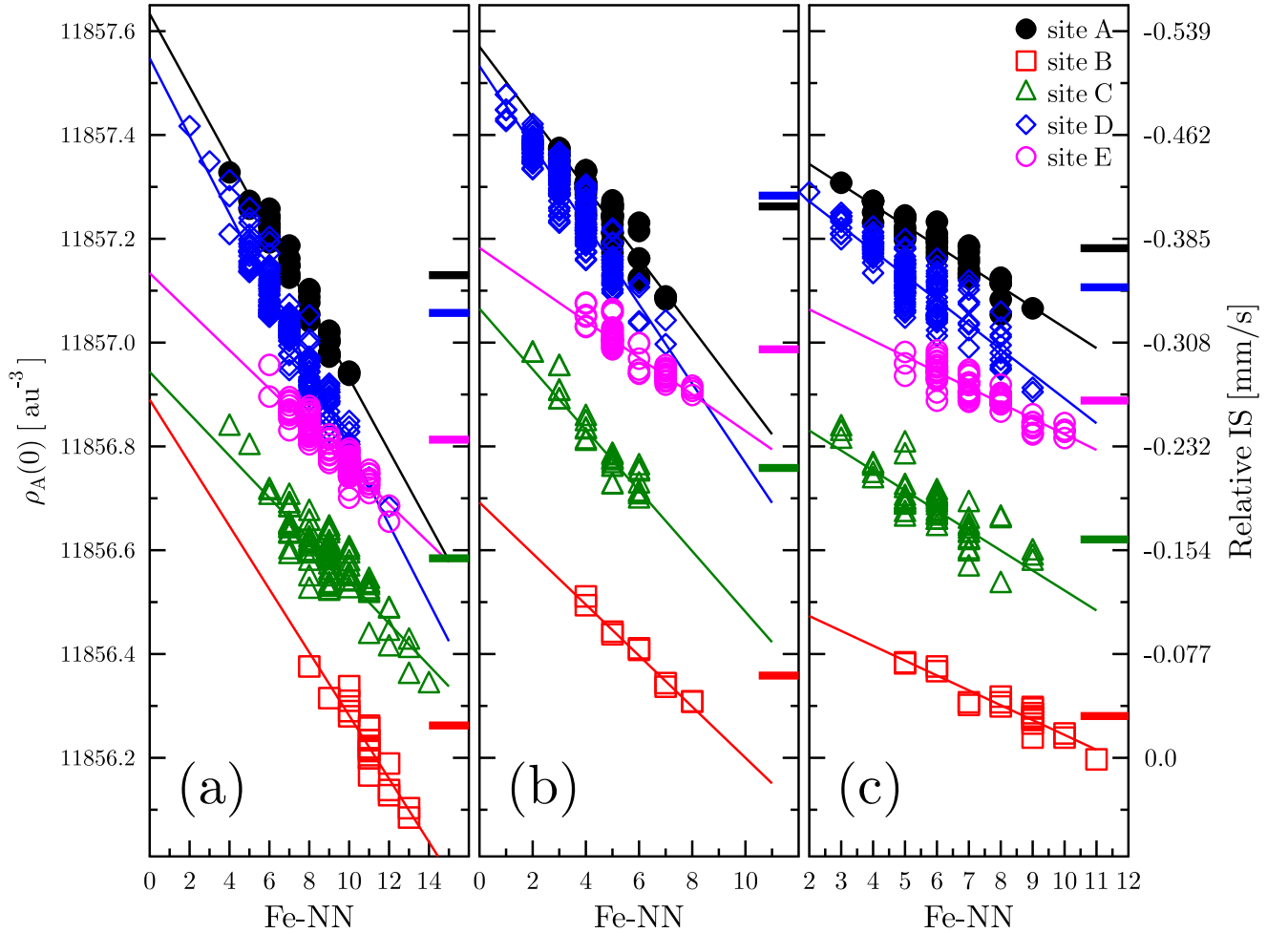


FIG. 1: (Online color) Fe-site charge-density,  $\rho_A(0)$ , for five crystallographic sites versus the number of NN-Fe atoms for (a)  $\text{Fe}_{66.7}\text{V}_{33.3}$ , (b)  $\text{Fe}_{40}\text{V}_{60}$  and (c)  $\text{Fe}_{54}\text{Cr}_{46}$ . The lines stand for the best linear fits to the data that represent  $\rho_A(0)$ -values for particular atomic NN-configurations. The average value of  $\rho_A(0)$  for each site is indicated by a horizontal bar on the right-hand axis on which are marked corresponding *IS*-values in mm/s.

adapted to investigate electronic structure of chemically disordered  $\sigma$ -phase as it occurs in the Fe-V system. However, such self-consistent calculations are very time-consuming due to the presence of Fe/V atoms disorder on all sites as well as a high multiplicity (8i) of three sites giving rise to a long process of CPA self-consistency cycles. In addition, such results may only give us the quantities averaged over all possible atomic configurations. This can be important when studying theoretically magnetic properties of these compounds, but it appears rather useless in the determination of the spectral parameters in the paramagnetic state. We have proposed an alternative approach to face the problem [11], in which the electronic structure of the  $\sigma$ -phase was calculated in a reasonably large number of ordered approximants, namely atomic configurations. These configurations should represent the most probable Fe and V arrangements in the disordered  $\sigma$ -phase unit cell and cover

wide range of the Fe-nearest neighbour (NN) numbers but account for the fact that some configurations are much less probable than others [11]. Consequently, we have taken into account those NN configurations whose overall probability was greater or equal 0.95. Such probability cut-off has permitted to significantly reduce the configurations number and diminish computation time to a reasonable level. In practice, all calculations were carried out using the lowest symmetry simple tetragonal unit cell ( $P1$ ), in which the atoms had the same positions as in the original symmetry group ( $P4_2/mnm$ ), but they were occupied either by Fe or V atoms. In the case of the  $\text{Fe}_{100-x}\text{V}_x$  alloys, where the  $\sigma$ -phase exists for  $33 \leq x \leq 60$ , two border compounds have been chosen, i.e.  $\text{Fe}_{20}\text{V}_{10}$  corresponding to  $x = 33.3$ , and  $\text{Fe}_{12}\text{V}_{18}$  equivalent to  $x = 60$ . In order to obtain the most probable atomic configurations that satisfy the condition on the nearest neighborhood appearing with the

overall probability  $\geq 0.95$ , it was enough to take into account 26 and 17 different configurations for the  $x = 33.3$  and  $x = 60$  compounds, respectively. More details on the calculations can be found elsewhere [11].

Fig. 1 presents the charge-density at  $^{57}\text{Fe}$  nuclei,  $\rho_A(0)$ , and the corresponding isomer shift,  $IS$ , calculated for the specified  $\sigma$ -phase compositions for nonequivalent sites. Analyzing all dependences one can come to the following conclusions: (i)  $\rho_A(0)$  is characteristic of each site and it linearly decreases with the Fe-NN number at a rate typical for each site and composition, (ii) the highest charge-density have the sites A and D, and the lowest one the site B, and the difference between them depends on the composition but hardly on the number of Fe-NN atoms, (iii) the value of the charge-density at a given site depends on the alloy composition. The decrease of the charge-density with the increase of the Fe-NN atoms observed for all sites and compositions means that there is an effective charge transfer from V atoms to Fe atoms. A similar effect was observed for disordered *bcc* Fe-V alloys [13]. Using a fitted scaling constant from [14], one can correlate the calculated charge-densities with the number of *s*-like electrons. Thus the average charge density at Fe nuclei on the site A is equal to 0.175 for  $x = 33.3$  and to 0.205 *s*-like electrons for  $x = 60$ . For site B the corresponding values are 0.013 and 0.031. It is also interesting to estimate in this way the difference in the charge-density between the extreme sites i.e. A and B. By doing so one arrives at 0.162 for  $x = 33.3$  and 0.174 for  $x = 60$  i.e. the difference hardly depends on the composition.

The charge-densities for any other  $x$ -value lying between 33.3 and 60 can be determined as a weighted average of the parameters obtained for the two border compositions. Taking into account  $IS$ -values calculated for different compositions, atom configurations and sites one can calculate an average  $IS$ -value,  $\langle IS \rangle_i$  ( $i = A, B, C, D, E$ ) for each nonequivalent site. The  $\langle IS \rangle_i$  values obtained in this way are marked on the right-hand scale in Fig. 1 as horizontal bars. The probability of each site,  $P_i$  as well as the aforementioned  $\langle IS \rangle_i$  allow determining the average isomer shift for selected composition  $\langle IS \rangle$ ,

$$\langle IS \rangle = \sum P_i \langle IS \rangle_i \quad (1)$$

As illustrated in Fig. 2 theoretically calculated  $\langle IS \rangle$ -values are in a good agreement with the measured center shift,  $\langle CS \rangle$ . The data presented here also give a clear evidence that substituting Fe by V in the  $\sigma$ -phase structure has quite similar effect on the Fe-site charge-density values as already observed in the  $\alpha$ -phase structure [13], where it also increased the Fe-site charge-density.

The good agreement between the experimental and calculated data give us a confidence that our electronic structure calculations deliver reliable description of the

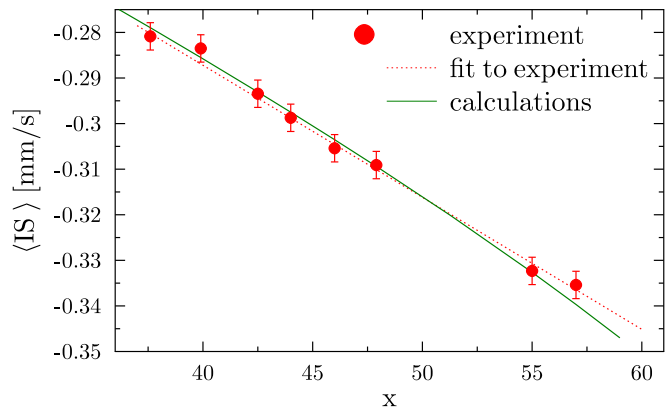


FIG. 2: (Online color) Average center shift,  $\langle CS \rangle$  versus vanadium concentration,  $x$ , as measured (circles) and as calculated (solid line). The dashed line indicates the best-fit to the measured values.

hyperfine parameters in the  $\sigma$ -phase samples. One may expect that a more detailed information obtained for the sublattice charge-density is also credible.

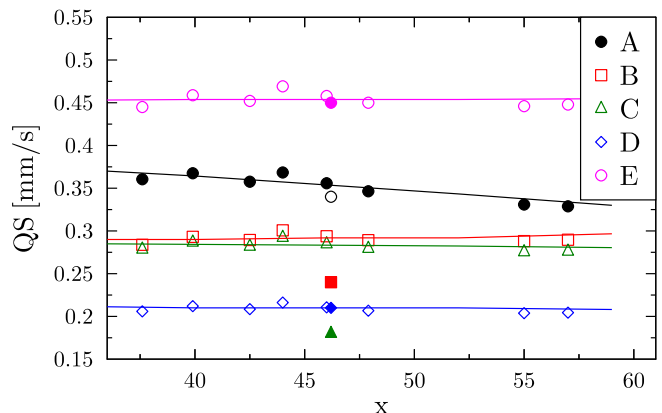


FIG. 3: (Online color) Quadrupole splitting,  $QS$ , as determined for each site and vanadium concentration,  $x$ , from the analysis of the measured spectra with the protocol described in the text. Values obtained previously for a  $\sigma$ -Fe-Cr compound are indicated as reversely-filled symbols for comparison.

Concerning the second spectral parameter i.e.  $QS$ , it was calculated based on an extended point charge model as described in detail elsewhere [11]. The obtained  $QS$ -values for each site and composition are shown in Fig. 3. It is clear from the figure that also  $QS$  is characteristic of each site, maybe except for the sites B and D for which  $QS$ -values are very close to each other whatever the concentration  $x$ . Another interesting feature is that except for the A site the  $QS$ -values remain constant vs. composition for all sites. The greatest  $QS$ -value was found for site E ( $\sim 0.45$  mm/s) and the lowest one for C ( $\sim 0.20$  mm/s). For comparison,  $QS$ -values obtained previously for the  $\sigma$ -Fe-Cr compound [11] are marked by reversely-

filled symbols in Fig. 3. Interestingly, for the sites A, C and E they match very well the values calculated in the  $\sigma$ -Fe-V, while for the sites B and D they are significantly smaller and differ one from another. Finally, using for the relative intensities of the five subspectra the values as found from the neutron diffraction experiment [12] on one hand, and taking for  $IS$  and  $QS$  the values obtained from the present calculations on the other hand, we have successfully refined the measured  $^{57}\text{Fe}$  Mössbauer spectra. In the fitting procedure, each subspectrum was regarded as composed of double lines with the same  $QS$  and  $IS$ -values linearly dependent on the number of the Fe-NN atoms and probabilities obtained from the binomial distribution. It should be mentioned that only five free parameters were needed for the analysis, i.e. background, total spectral area,  $IS$  for site B (to adjust the refined spectrum to the used source of the gamma rays), line width and a proportionality factor between  $QS$  and an energy shift due to the quadrupole interactions [11]. The agreement between the experimental and calculated spectra is excellent for all measured compositions of the  $\sigma$ -Fe-V system.

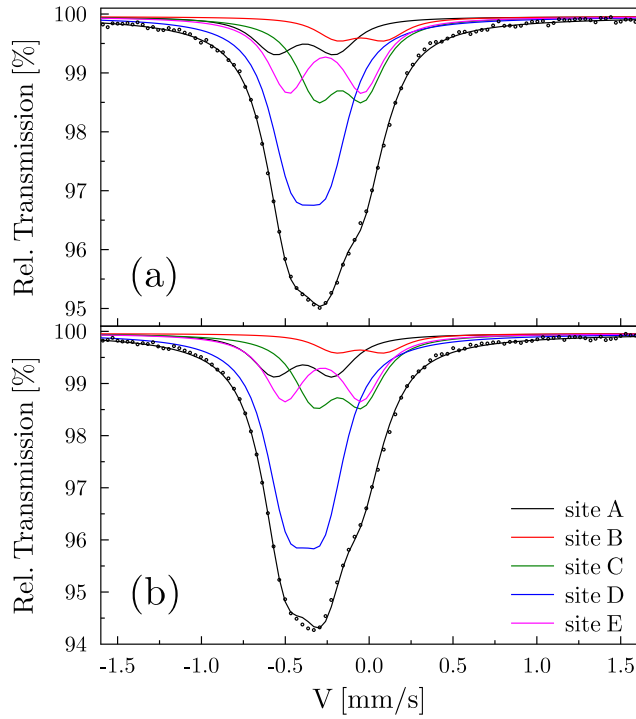


FIG. 4: (Online color)  $^{57}\text{Fe}$ -site Mössbauer spectra recorded at 295 K on two samples with (a)  $x = 37$  and (b)  $x = 46$ . The best-fit spectrum and five subspectra are indicated by solid lines.

In summary, our results of the KKR electronic structure calculations obtained for the  $\sigma$ -Fe-V system lead to conclusion that the proposed procedure, based on the hyperfine parameters calculated from the first principles in

combination with the experimental data for the atom distribution over the five sublattices, gives information on the charge-density and the electric field gradient in the complex disordered alloy system. It should be mentioned here, that this information was obtained for all five sublattices separately, taking into account the real atomic concentrations on them.

The progress and advantage of our calculations in comparison to those carried out by others, in which homogeneously occupied sublattices were considered, is that we have taken into account much more various atomic configurations that has enabled us to get more deep, precise and realistic insight into the electronic structure of the  $\sigma$ -phase. Our calculations have been, in addition, verified by a comparison with experimental data. A very good agreement achieved can be taken as evidence that the procedure we have applied gives a good approach to the real electronic structure of the studied system. It can be also of a practical importance while analyzing ill-resolved Mössbauer spectra recorded on samples with a complex structure.

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